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VACANCY DISTRIBUTION AND MAGNETIC ORDERING IN IRON SULFIDES

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The vacancy distribution and types of magnetic ordering in iron sulfides in the $\square_x Fe_{1-x}S$ system ($0.091 \leq x \leq 0.119$) are studied by the nuclear gamma-resonance technique. The hyperfine structure components are ascribed to structurally and magnetically nonequivalent iron positions which differ in the number of vacancies in their immediate vicinity. It is shown that the $Fe_{0.881}S$ phase is ferrimagnetic with long-range order in the vacancy distribution (NiAs structure with monoclinic distortion). In hexagonal (NiAs type) $Fe_{0.900}S$, the ferrimagnetic properties are ascribed to coexistence of ordered and disordered states within a single phase. Below a certain minimal vacancy concentration ($x \leq 0.096$) the ordered state is completely destroyed and the substances become antiferromagnetic. Transformation of the antiferromagnetic phase $Fe_{0.909}S$, into a ferrimagnetic one (anti-Curie point) is accompanied by partial vacancy ordering in the absence of long-range order, as in the case of $Fe_{0.900}S$.

1. INTRODUCTION

IRON sulfides $\square_x Fe_{1-x}S$ ($0 \leq x \leq 0.125$; $\square$ denotes a vacancy[1,2]) have no unified magnetic structure and differ in the type of magnetic ordering depending on the vacancy content x. The group of sulfides with $0.04 \lesssim x \lesssim 0.1$ is characterized by a hexagonal close-packed anion matrix, in the octahedral interstices of which the iron ions are located (structure of the NiAs type).[1] Indirect (or superexchange) cation-anion-cation interactions lead to mutually antiparallel orientation of the electron spins in alternating layers parallel to the basal plane.[2] Such sulfides are antiferromagnetic.

Compounds with a smaller content of iron, and consequently with a larger number of vacancies (the group with $0.1 \lesssim x \leq 0.125$) have spontaneous magnetization with a Curie temperature T_C that increases with increasing x.[1] In interpreting the ferrimagnetic properties of the last compound of this group, Fe_7S_8 ($x = 0.125$), Bertaut proposed[3] that the vacancies are arranged in the iron positions in an orderly fashion, repeating in each second layer of cations. As a result of the difference in the numbers of iron ions with oppositely directed spins, an uncompensated magnetic moment is produced. For intermediate compositions of this group ($0.1 \lesssim x < 0.125$), we know of no published data on the distribution of the vacancies and on the magnetic structure.

We present in this paper the results of investigations of natural sulfide crystals $\square_x Fe_{1-x}S$ (pyrrhotines) in the concentration interval $0.091 \leq x \leq 0.119$ by the Mossbauer method. It was of interest to investigate the distribution of the vacancies in the pyrrhotines and the influence of this distribution in the crystal structure and on the character of the magnetic ordering.

The γ-resonance spectra of the sulfides revealed a transition from a hexagonal structure to a monoclinic one with increasing vacancy concentration. At intermediate vacancy concentrations ($x \sim 0.1$), we observed a partial ordering of the vacancies, namely, alternation of layers having vacancies with layers containing no vacancies.

We present in this article three typical γ-resonance spectra corresponding to three different types of vacancy distribution in pyrrhotines. Principal attention has been paid to an investigation of the dependence of the parameters of the magnetic hyperfine structure (hfs) of the γ-resonance spectra on the vacancy concentration and distribution. We discuss the relation between this distribution and the type of magnetic ordering. Certain samples were additionally investigated by the x-ray diffraction method.

2. EXPERIMENT

We chose for the investigations a group of natural $\square_x Fe_{1-x}S$ crystals. The relative concentration of the iron in these crystals was determined from the interplanar distance d_{102} on the basis of an analysis of the diffraction patterns obtained with the URS-50 diffractometer. We used the K_α line of iron. The dependence of the content of the metal (Fe) in the sulfide on the value of d_{102} was approximated by a second-degree polynomial, the coefficients of which were determined by least squares from the experimental data.[4,5]

The obtained dependence was used to determine the composition of the sulfides having a hexagonal structure. In those cases when the diffraction patterns contained lines corresponding to the monoclinic structure, the samples (naturally, after obtaining the Mossbauer spectra), were heated (15 hours) to 600°K in evacuated quartz ampoules and were subsequently quenched. This transformed the monoclinic sulfide into hexagonal. The absence of a monoclinic phase was verified by using the magnetic powder-pattern method and measuring the microhardness and the reflectivity of the samples processed in this manner.

The sample $Fe_{0.881}S$ had a monoclinic structure with a superstructure of the type 4c characteristic of the ordered Fe_7S_8.[3] The remaining compositions were hexagonal with a lattice of the NiAs type. The γ-resonance spectra were plotted at room temperature using a spectrometer with an electrodynamic vibrator. The source was $Co^{57}(Cr)$. To determine the type of the magnetic structure of the sulfides, external magnetic fields were also used when plotting the Mossbauer spectra.

The γ-resonance spectra of sulfides with different compositions (Figs. 1a–c) present a complicated picture of superposition of several Zeeman sextuplets. In a relatively small interval of vacancy concentrations, the three-component resolved magnetic hfs characteristic of $Fe_{0.881}S$ (A, B, and C of Fig. 1a) goes over into an unresolved structure with broadened lines ($Fe_{0.909}S$, Fig. 1c). In the case of the first two compositions (Figs. 1a, b) the splitting and relative intensity of component A of the hfs remain practically unchanged. At the same time, the relative intensities of the other components change radically in these two spectra. Additional components with close parameters appear.

3. DISCUSSION

In the interpretation of the γ-resonance spectra we made the following assumptions: 1) each group of fixed lines in the Mossbauer spectrum corresponds to a definite position of the iron, characterized by the same number of vacancies in the nearest neighboring sites; 2) in counting the number of nearest neighbors, it suffices to take into consideration only those with which the given ion forms indirect exchange bonds; 3) the minimum hyperfine magnetic field pertains to cations having the maximum number of vacancies in the nearest neighbors; 4) the probabilities of the possible configurations of the nearest surrounding of the iron, at a statistical distribution of the vacancies, are determined by a binomial law (similar to that described in [6]); 5) the investigated compositions are single-phase.

Computer reduction of the spectra within the framework of the foregoing assumptions has resulted in a satisfactory agreement with the experimental data.

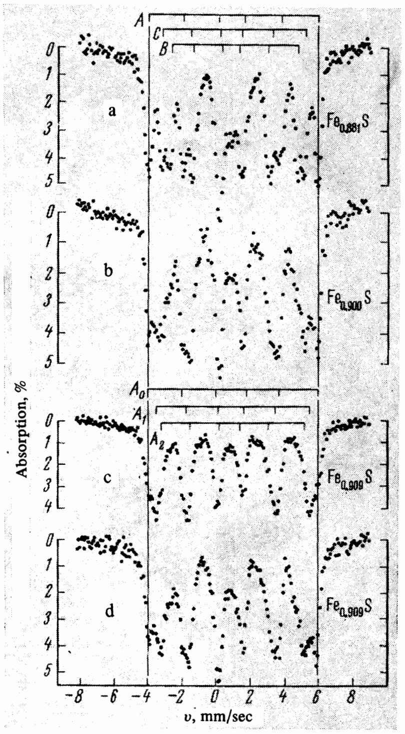

FIG. 1. Gamma-resonance spectra of compounds of the system $\square_x Fe_{1-x}S$ (T = 300°K): a–x = 0.119, b–x = 0.100, c–x = 0.091, d–spectrum after quenching the sample with x = 0.191 from the temperature T of the phase transition. The position of the lines of the magnetic hyperfine structure components (A, B, C and A_0, A_1, A_2) are separated. The vertical lines running through the entire picture represent the positions of the first and sixth lines of the A component of the hyperfine structure.

1. Distribution of Vacancies and Hyperfine Field in $Fe_{0.881}$ S

The sulfide $Fe_{0.0881}S$ has a monoclinic structure and is close in composition to the ordered Fe_7S_8. The crystal structure of Fe_7S_8 is shown in Fig. 2.[3,7] The ordering of the vacancies in the iron positions corresponds to the space group C2/c. A sulfide of this composition has a pseudohexagonal unit cell with small monoclinic distortion. The cell contains four Fe_7S_8 molecules. The sulfur ions are arranged between the cation layers in such a way that each iron atom is coordinated octahedrally. The sulfur positions are shown in the projections of the two neighboring planes of the unit cell. The iron ions occupy four nonequilibrium positions 4e, $8f_1$, $8f_2$, $8f_3$, with population ratio $\frac{1}{2}:1:1:1$. The crystallographic nonequivalence of the positions is due to the difference in the number of cations and vacancies in the nearest surrounding.

The indirect exchange coupling is realized between cations of neighboring planes (coupling angle ~ 135°) and leads to antiferromagnetic orientation of the magnetic moments of the nearest neighbors.[2] The weaker interactions within the plane, and also the direct cation-cation interactions between the planes, can be neglected.[2,7] From this point of view, the iron ions in positions 4e and $8f_1$ have no vacancies among the nearest neighbors and are coupled by 12 exchange couplings (6 above and 6 below) with the $8f_2$ and $8f_3$ cations. The iron ions in the positions $8f_2$ and $8f_3$ have in the immediate surrounding 4 and 2 vacancies, respectively, and are characterized by 8 and 10 exchange couplings.

Thus, the positions 4e and $8f_1$ are magnetically equivalent and therefore have identical parameters of the hyperfine interaction on the Mossbauer spectrum (A component of the hfs, Fig. 1a). This relation is confirmed by the fact that the hfs parameters of stoichiometric FeS (x = 0),[8] where all the cations are equiv-

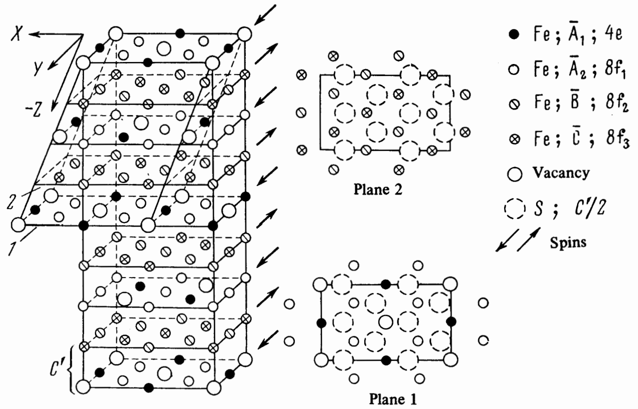

FIG. 2. Pseudohexagonal structure of Fe_7S_8 according to Bertaut [3]. The iron ions are located at the centers of distorted octahedra of sulfur ions. The sulfur positions are shown in the projections of the two neighboring planes.

alent, are close to the parameters of the A component of the $Fe_{0.881}S$ under consideration. The presence of vacancies in the nearest neighbors of the positions $8f_2$ and $8f_3$ leads to a decrease of the hyperfine fields (B and C components of the hfs). The ratios of the component intensities I_i, A : B : C = 1.5 : 1 : 1, that follow from the given model are comparable with those observed in experiment (1.34 : 1.00 : 1.02, see the table). Thus, the sextuplets A, C, and B pertain to iron ions which have 0, 2, and 4 vacancies, respectively, in the nearest surrounding.

The dependence of the magnitude of the hyperfine field on the number of vacancies among the nearest neighbors may be due to different exchange energies, and consequently to a difference in the mean value of the spin of the iron ($\langle S_i \rangle$) in each of the positions (at $T/T_C \sim 0.5$).[9] A contribution to the hyperfine field may come also from the hyperfine interaction transferred through the sulfur iron,[10] but its magnitude is indeterminate.

2. Ordering of Vacancies in $Fe_{0.900}S$

The system $\Box_x Fe_{1-x}S$ has been the subject of a rather large number of investigations. The question of the vacancy distribution in those cases when their concentration does not correspond to a fully ordered structure,still remains unclear. The x-ray procedure customarily used for the investigation of this system describes the crystal structure only from the point of view of the long-range order singularities. Magnetic measurements do not yield direct information on the microstates of the iron ions. Short-range order effects can be investigated only by procedures that are sensitive to the singularities of the microstate of an individually taken atom or ion, particularly by the method of nuclear γ resonance.

The x-ray diffraction pattern of $Fe_{0.900}S$ (which is not included here), can be interpreted as a sum of the diffraction patterns of two phases (~ 80% hexagonal and ~ 20% monoclinic). But the γ-resonance spectrum (Fig. 1b) is not a simple superposition of the spectra of the purely hexagonal (Fig. 1c, $Fe_{0.909}S$) and monoclinic (Fig. 1a, $Fe_{0.881}S$) phases.

The experimental spectrum of $Fe_{0.900}S$ contains two intense sextuplets that coincide with the components A and C of the $Fe_{0.881}S$ spectrum (Fig. 1). These two components correspond to iron ions with zero and two vacancies, respectively. Thus, it can be assumed that in the case of $Fe_{0.900}S$, these two types of surroundings are most probable.

Characteristics* of γ-resonance spectra of iron sulfides

hfs Components	I_i	H_i, kOe	δ_i, mm/sec	Δ_i, mm/sec
		$Fe_{0,881}S$		
A	1.34±0.1	305±3	+0.47±0.01	+0.31±0.03
B	1.00±0.1	224±3	+0.45±0.02	+0.43±0.04
C	1.02±0.1	253±4	+0.44±0.02	+0.31±0.04
		$Fe_{0,909}S$		
A_0	0.33±0.05	302±10	+0.58±0.08	+0.23±0.1
A_1	0.44±0.05	274±10	+0.58±0.1	+0.00±0.1
A_2	0.23±0.05	256±10	+0.57±0.1	+0.30±0.1

*The intensities I_i of the γ-resonance spectra of the magnetically-nonequivalent iron positions, the hyperfine magnetic fields H_i, the isomer shift δ_i (relative to sodium nitroprusside), and the quadrupole splittings Δ_i, obtained at 300°K.

At the same time, for a random distribution of the vacancies in the $Fe_{0.900}S$ composition, the probabilities P_n of the possible states of the iron ions with n vacancies in the nearest surrounding are equal to $P_0 = 0.32$, $P_1 = 0.42$, and $P_2 = 0.26$. The three most intense components should be in this case those corresponding to 0, 1, and 2 vacancies, and not to 0 and 2.

Indeed, besides the two noted components (A and C components—0 and 2 vacancies), the spectrum contains at least two more sextuplets. One of them has a hyperfine field value intermediate between 305 (0 vacancies) and 253 (2 vacancies) kOe and corresponds obviously to iron ions having one vacancy in the surrounding. The first and sixth lines of this sextuplet lie between the corresponding lines of the components A and C, leading to a deterioration in the resolution of the hfs spectra. In addition, on the internal slopes of the lines of component C one can see additional lines of the fourth sextuplet with a hyperfine field value less than 240 kOe. Obviously, this sextuplet pertains to the iron ions having more than two vacancies.

The relative populations of the cation sites with different numbers of vacancies can be explained by assuming that in the $Fe_{0.900}S$, at a corresponding concentration of the intruded iron ions (on top of Fe_7S_8), the order of the arrangement of the vacancies inside the cation layers is violated completely or in part, but the alternation of the layers with and without vacancies remains undisturbed (see Fig. 2).

We note that the iron ions located in planes containing vacancies retain the nearest-surrounding configuration characteristic of the fully ordered structure. The corresponding parameters of the hyperfine interaction practically coincide with the parameters of the A component of the hfs in Fe_7S_8 (Figs. 1a, b).

The described type of partly ordered structure explains the ferrimagnetism of $Fe_{0.900}S$[1] and is confirmed by the measurements described below in an external magnetic field (item 4 of this section).

The seeming discrepancy between the x-ray diffraction and Mossbauer data can be attributed to the noted singularities of the partially-ordered structure, which make the interpretation of the diffraction patterns ambiguous.

3. Vacancy Distribution in $Fe_{0.909}S$

According to the x-ray data, $Fe_{0.909}S$ has a hexagonal structure. No monoclinic-phase impurities were observed. The γ-resonance spectrum differs strongly from the preceding spectra and consists of several unresolved sextuplets with close-valued parameters.

A similar form of the spectrum was observed by us for compositions starting with x = 0.096 ($Fe_{0.904}S$) and below. Obviously, below a certain minimum vacancy concentration, their ordered state is disturbed. The small relative intensity of the A sextuplet is direct evidence that the structure no longer contains alternating layers with and without vacancies.

The γ-resonance spectrum of $Fe_{0.909}S$ (Fig. 1c) is approximated by a superposition of three sextuplets with intensity ratio 0.33 : 0.44 : 0.23 (see the table). If the vacancies are randomly distributed, then the probabilities of the appearance of 0, 1, and 2 vacancies among the 12 nearest neighbors of iron are respectively 0.35, 0.42, and 0.23, in good agreement with the relative intensities of the components A_0, A_1, and A_2, which we ascribe to positions with 0, 1, and 2 vacancies. It is remarkable that the hfs parameters of the corresponding components of the ordered phase ($Fe_{0.881}S$) and of the disordered phase ($Fe_{0.909}S$) (A and A_0, C and A_2, see the table) coincide.

4. Connection Between the Vacancy Distribution and the Magnetic Properties of the System $\square_x Fe_{1-x}S$

The magnetic properties of the system $\square_x Fe_{1-x}S$ were investigated by many researchers.[1, 11-15] It has been shown that the system has an uncompensated magnetic moment if the vacancies are ordered, and is antiferromagnetic if the order of the vacancies is disturbed. It is also known that the same composition can have either an ordered or a disordered vacancy distribution, depending on the temperature. These conclusions were drawn from the jump of the magnetic susceptibility and confirmed by x-ray investigations. Thus, the magnetic and structural transformations are conjugated.

The use of external magnetic fields while plotting the γ-resonance spectra has made it possible to compare the structure and magnetic properties of the sulfides investigated by us. The measurements were performed at $H_{ext} = 17$ kOe perpendicular to the propagation direction of the γ quanta. The spectra ($T = 300°$) are shown in Figs. 3a–c.

In the spectrum of $Fe_{0.881}S$ (ordered structure) there is observed an increase of the hyperfine splitting of the A component and a decrease of this splitting for the B and C components. It follows therefore that the magnetic moments of the B and C sublattices are parallel to each other and are opposed to the moment of the A sublattice.[1)] The summary moment of the B and C sublattices is larger than the moment of the A sublattice.

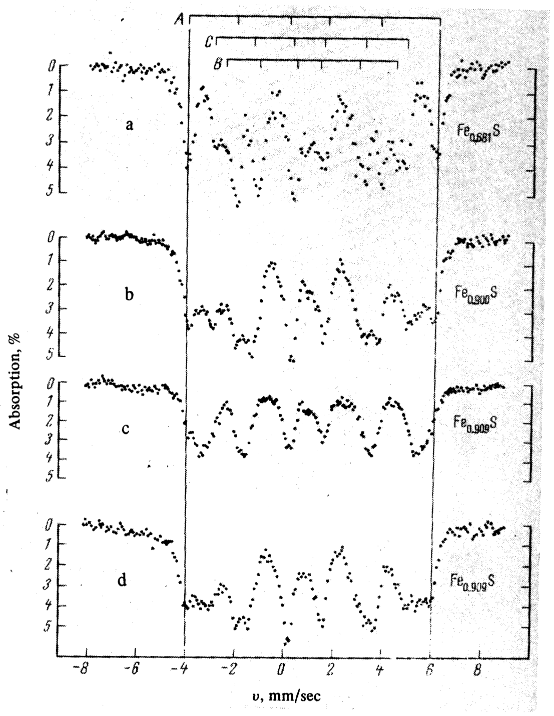

FIG. 3. Gamma-resonance spectra of compounds of the system $\square_x Fe_{1-x}S$ for different x in an external magnetic field $H_{ext} = 17$ kOe perpendicular to the γ-quantum beam; T = 300°K. The symbols are the same as in Fig. 1.

The results agree with the present notions concerning the crystalline and magnetic structures of Fe_7S_8.[3,7] The system constitutes a sequence of ferromagnetic planes of two types, including alternately either only A cations or only B and C cations. The magnetic moments of the planes of these two types have opposite directions (Fig. 2).

The variation of the spectrum of $Fe_{0.900}S$ when the sample is placed in an external magnetic field is similar (Fig. 3b). The hyperfine splitting of the A component increases and the splitting of the remaining components of the spectrum decreases. The lines become broader. This also confirms the ferrimagnetic structure of $Fe_{0.900}S$, which is a result of a layer-by-layer ordered arrangement of the vacancies.

In the case of the antiferromagnetic $Fe_{0.909}S$ in an external magnetic field (Fig. 3d), one observes the broadening of the hfs lines typical of antiferromagnets, without a shift of their centers of gravity. Each of the three nonequivalent positions of the iron (A_0, A_1, and A_2, which differ in the number of vacancies in the nearest neighbors), constitutes separately an aggregate of two antiferromagnetic subsublattices. Missing from the spectrum of Fig. 3d are not only shifts of the hfs lines, but also noticeable changes in their relative intensities.

The ferrimagnetic compounds $\square_x Fe_{1-x}S$ are characterized by a sharply pronounced anisotropy of the magnetic properties in the direction of the hexagonal axis.[2)] This explains, in addition to the line broadening, also the fact that in an external magnetic field (Figs. 3a, b) the observed average shift of the hyperfine field is

$$\Delta H = \frac{2}{\pi}\int_0^{\pi/2} H_{\text{ext}}\cos\theta\, d\theta = \frac{2}{\pi} H_{\text{ext}}$$

where θ is the angle between the magnetization of the individual crystallite and the direction of $\mathbf{H}_{ext}$.

Let us note one more important feature of the investigated system. A decrease of the vacancy concentration in the ferrimagnetic compositions ($Fe_{0.881-0.901}S$) leads to an increase in the average number of exchange couplings per magnetic ion. This, in turn, should be accompanied by an increase in the exchange energy and the Curie temperature T_C of the system. However, the experimental data indicate the opposite: T_C decreases from 573°K for Fe_7S_8 to 535°K for $Fe_{0.9}S$.[1]

This regularity is obviously connected with the distinguishing features of magnetically-ordered interactions in iron sulfides. As shown in [7, 19], the charge

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[1)] The hyperfine field at Fe^{57} nuclei is negative [16].

[2)] The anisotropy energy in the direction of the c axis of Fe_7S_8 is $\sim 10^7$ erg/cm^3 [17], and cannot be explained in accordance with the scheme of dipole-dipole coupling of the magnetic moments [18]. The source of the magnetic anisotropy in this case may be the anisotropy of the indirect exchange interactions. It follows directly from the geometry of the exchange couplings in the structure of Fe_7S_8 (see Fig. 2), that the Fe-S-Fe indirect exchange coupling is realized between cations in neighboring planes and is quite weak within the planes.

state of the iron ions in nonstoichiometric $Fe_{1-x}S$ compounds is close to Fe^{2+}. Deviation of the composition from stoichiometric apparently leads to a uniform distribution of the excess electric charge among the cations.[7] It follows therefore that when the iron content in $Fe_{1-x}S$ increases, the average charge decreases, and with it also the effective spin S_{eff} of the iron ions. Apparently the effect of increasing the number of exchange couplings is offset by the stronger decrease of the energy of each individual superexchange coupling as a result of the decrease of S_{eff}.

The observed change in the temperature of the magnetic ordering can be explained on the basis of a quantitative analysis of all types of magnetic interactions in which iron ions participate. We note here that the iron ions in the sulfides $\square_x Fe_{1-x}S$ also have other features that distinguish them from the "ordinary" divalent iron compounds (for example, a weak dependence of the isomer shift and of the quadrupole splitting on the temperature[19]).

5. Transformation of the Antiferromagnet–Ferrimagnet Type in $Fe_{0.909}S$

The connection and mutual influence of structural and magnetic transformations in the $\square_x Fe_{1-x}S$ system can be clearly illustrated with the example of the transformation that occurs in $Fe_{0.909}S$ at a certain temperature T_γ, called the anti-Curie point. Such transformations are characteristics of the system in the interval $0.07 \leq x \leq 0.09$ and are transformations of the antiferromagnetic structure into a ferrimagnetic structure.[14] This transformation is connected with the ordering of the vacancies and is reversible.[1, 14, 15]

The phase $Fe_{0.909}S$ is antiferromagnetic (the vacancies are disordered) at room temperature, becomes ferrimagnetic (the vacancies are ordered) at temperatures from $T_\gamma = 453°K$ all the way to the Curie point. Such a phase was obtained by us after annealing the sample in an inert atmosphere at 489°K and subsequent quenching in liquid nitrogen.

The spectrum of the quenched sample is shown in Fig. 1d. Unlike the initial spectrum (Fig. 1c), in this case there is splitting of the outermost hfs lines into two components. In an external magnetic field $H_{ext} = 17$ kOe, one observes motion of the components in opposite directions: the outer one moves towards increasing hyperfine field, and the internal one in the opposite direction (Fig. 3d). This proves the presence of ferrimagnetism in the quenched phase $Fe_{0.909}S$ and layered ordering of the vacancies. The structure of the spectrum (Fig. 1d) and the character of its variation (Fig. 3d) in an external magnetic field are very close to the spectrum of $Fe_{0.900}S$ (Figs. 1b and 3b). We can therefore conclude that at the temperature T_γ there occurs a partial ordering of the vacancies, in analogy with that present in $Fe_{0.900}S$ at room temperature.

The quenched phase is metastable. Upon heating to the transformation temperature T_γ and subsequent slow cooling, the phase again becomes antiferromagnetic and its spectrum becomes identical with the initial one (Fig. 1c). We note that storage of the quenched sample for three months at room temperature also leads to a disordering of the vacancies and to a transition into the antiferromagnetic state. On the other hand, the partially ordered compositions $Fe_{0.898}S$, $Fe_{0.900}S$, and $Fe_{0.901}S$ are stable. An analogous heat treatment (heating to T_γ with subsequent quenching or slow cooling) did not lead to a vanishing of the ferrimagnetic state or to an appreciable change in the form of the γ-resonance spectra.

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